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### Kinetics of Oxidation of Formic Acid by Chromic Acid in Phosphoric Acid Medium

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Received 31 March 1977; accepted 22 June 1977

Kinetics of oxidation of formic acid by chromic acid is studied in moderately high concentrations of phosphoric acid (1.0 to 7.0M). The reaction has been found to be first order in either of the reactants. In the concentration range of 6.0-7.0M, a pronounced rate enhancement has been observed. The linear proportionality observed between the rate and the concentration of formic acid can be employed for the analytical determination of small amounts of formic acid.

THE oxidizing ability of potassium dichromate is reported<sup>1</sup> to increase to a great extent in high phosphoric acid medium. The oxidation kinetics of formic acid by chromium(VI) in phosphoric acid has not received much attention eventhough similar studies in other acids are fairly extensive<sup>2-9</sup>. Mahajani<sup>10</sup> investigated the reaction in the presence of only low concentrations (0.02 to 1.1M) of phosphoric acid and reported that phosphoric acid in this concentration range behaves like acetic acid or hydrochloric acid or sulphuric acid. We present in this note our kinetic results on formic acid oxidation by Cr(VI) in moderately high concentrated solutions of phosphoric acid (1.0 to 7.0M).

Reagent grade chemicals were used in the study. The solutions were prepared in triply distilled water. The reaction was monitored photometrically using ELICO Spectrocol model CL-23 by estimating unreacted Cr(VI) at 450 nm. Beer's law is obeyed in the concentration range of Cr(VI) employed. The pseudo-first order rate constant ( $k$ ) was computed from the linear plot of  $\log$  (absorbance) vs time after appropriate correction for the absorbance of Cr(III) at 450 nm. Kinetic runs were reproducible within  $\pm 2\%$ .

The reaction was found to be first order in formic acid and Cr(VI). This can be employed for the analytical determination of small amounts of formic acid.

The values of pseudo-first order rate constant ( $k$ ) at different [phosphoric acid], presented in Table 1, show that the rate constant increased with [phosphoric acid] in the entire range of study. However, the magnitude of increase in rate is very much

TABLE 1 — PSEUDO-FIRST ORDER RATE CONSTANT ( $k$ ) AT VARIOUS ACID CONCENTRATIONS FOR THE OXIDATION OF FORMIC ACID BY Cr(VI)

{[Cr(VI)]= $2.3 \times 10^{-3}M$ ; [HCOOH]= $7 \times 10^{-1}M$ ; temp.= $30^\circ$ }

[H <sub>3</sub> PO <sub>4</sub> ] M	$k \times 10^6$ sec <sup>-1</sup>	[H <sub>3</sub> PO <sub>4</sub> ] M	$k \times 10^6$ sec <sup>-1</sup>
1.0	7.2	5.0	122.2
2.0	16.6	5.5	219.4
3.0	29.7	6.0	417.8
4.0	62.6	6.5	565.3
4.5	93.7	7.0	1515.0

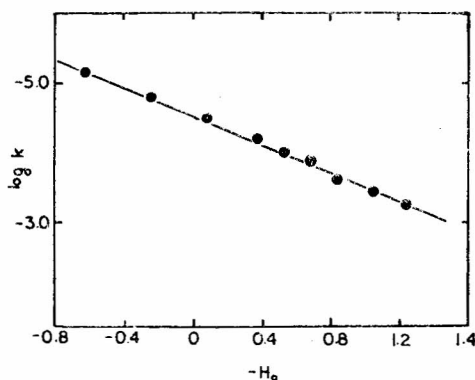


Fig. 1 — Plot of  $\log k$  versus Hammett acidity function ( $-H_0$ ) for the oxidation of formic acid by Cr(VI) in H<sub>3</sub>PO<sub>4</sub>.

higher at [H<sub>3</sub>PO<sub>4</sub>] > 5.0M. Plot of  $\log k$  vs  $\log$  (molarity) of the acid consisted of two linear portions with slopes of about 2 and 8 respectively. These facts may have to be attributed to the different chromium species in the two ranges of phosphoric acid.  $\log k$  varied linearly with Hammett acidity function ( $-H_0$ ) and the slope is unity (Fig. 1). This suggests an A-1 type of mechanism. The plots of  $1/k$  against  $1/[H_3PO_4]$  and  $1/k$  against  $1/[HCOOH]$  are linear, with an intercept. This according to Michaelis-Menten relation indicates that complex formation step between Cr(VI) and formic acid precedes the rate limiting step.

The activation parameters  $\Delta E^*$  and  $\Delta S^*$  are 49.7 J deg<sup>-1</sup> mol<sup>-1</sup> and -150 J deg<sup>-1</sup> mol<sup>-1</sup> at 4.5M acid and 36.4 J deg<sup>-1</sup> mol<sup>-1</sup> and -197 J deg<sup>-1</sup> mol<sup>-1</sup> at 6.0M acid.

The authors are thankful to the CSIR, New Delhi, for the award of a junior research fellowship to one of them (C.O.R.).

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